

**Electron Impact Excitation of  $C_{60}$  Adducts;  
Fluorescence from  $C_{60}OH$  and  $C_{60}H$  Species**

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## Abstract

An investigation concerning possible visible and U V photon emissions by gas phase  $C_{60}$  (and  $C_{70}$ ) samples under electron impact excitation was carried out in the 180-750 nm spectral region. Radiation resembling OH I ( $A^2\Pi - X^2\Sigma$ ) emission bands and H Balmer series was observed. Based on our investigations, it is concluded that none of the observed emission was associated with the fullerene molecule itself but with  $C_{60}OH$  and  $C_{60}H$  adducts (which are present in the fullerene samples). We also conclude that in these adducts, simultaneous ionization and excitation take place under electron impact and the excited ionic species ( $C_{60}^+OH^*$  and  $C_{60}^+H^*$ ) decay by radiation which was observed in our experiments. These surprising results reveal an interesting new character of buckyball adducts. The thresholds of the  $C_{60}$  related 011 ((0)-0) transition and H Balmer  $\alpha$  radiation were found to be  $11.6 \pm 0.5$  and  $20.6 \pm 1.0$  eV, respectively. These values are  $2.4 \pm 0.5$  and  $3.4 \pm 1.0$  eV higher than the corresponding values associated with  $H_2O$ .

1 Discovery of the  $C_{60}$  (buckminsterfullerene or buckyball) molecule stimulated a great deal of interest in its physical and chemical properties. A number of investigations have been concerned with luminescence of  $C_{60}$  (and  $C_{70}$ ) in the condensed phases (pure solid and liquid solutions).<sup>1-6</sup> To our knowledge, no studies concerning electron-impact luminescence of gaseous  $C_{60}$  (and  $C_{70}$ ) have been reported. The initial aim of the present study was to fill in this gap in the visible and ultraviolet (UV) spectral regions. We investigated the 180 to 750 nm region for possible emission by  $C_{60}$  (and  $C_{70}$ ) samples as well as from their unenriched mixtures under electron impact and observed molecular band-type emission features in the 275 to 340 nm region and atomic-type emissions at longer wavelengths. These emissions were found to be similar to, but not identical with, OH emission bands and Balmer series lines from electron-impact dissociative excitation of  $H_2O$ . They are, however, remarkably different from the  $H_2O$  related emissions in several ways: The onset energy values and initial slopes of the excitation functions as well as the relative intensity distributions of the emission spectral features are significantly different.

Based on our investigations (described below), we came to the conclusion that  $C_{60}$  (and  $C_{70}$ ) does not emit radiation in the 180 to 750 nm wavelength region and that the observed emissions are associated with  $C_{60}OH$  and  $C_{60}H$  adducts. These species are formed during the production of the buckyball samples. Mass spectroscopic studies clearly show the presence of positive and negative ions associated with these adduct species in buckyball samples.<sup>7</sup> We conclude that in the loosely bound adducts, simultaneous ionization and excitation take place under electron impact and the excited ionic species ( $C_{60}^+OH^*$  and  $C_{60}^+H^*$ ) decay by radiation which is observed in our experiments. These surprising results reveal an interesting new character of buckyball adducts and give warnings that  $C_{60}$  and  $C_{70}$  samples are not homogeneous pure compounds and therefore, therefore, caution has to be taken in assigning observed characteristics of these samples.

A crossed electron-molecular beam configuration was used in the present studies of vapor phase buckyballs ( $C_{60}$ ,  $C_{70}$  and their mixtures procured from Materials and Electrochemical Research Corporation). Most of the studies were carried out with  $C_{60}$  sample. A stainless steel crucible was filled with the sample and a beam was formed by heating the crucible to about  $500^{\circ}\text{C}$ . The temperature of the crucible was monitored by a Chromel-Alumel thermocouple. The buckyball vapor effused through a 0.75 mm diameter hole, and formed a target beam without further collimation. Other target species He,  $N_2$ ,  $H_2O$ , etc., could be introduced into the interaction region through a capillary tube. An electron gun with magnetic collimation, similar in design to the one used by Ajello et al.<sup>8</sup>, was employed for the present measurements. An approximately uniform magnetic field, parallel to the electron beam and with a strength of 120 Gauss in the interaction region, was produced by four Alnico V bar magnets. The target beam was crossed at  $90^{\circ}$  by the electron beam at a distance about 0.5 cm from the point of effusion. The electron beam current ranged from a few to 100  $\mu\text{A}$  as a function of impact energy in various excitation function measurements and was very nearly constant in all spectral measurements. The electron beam current was monitored by a Faraday cup. The energy resolution [full width at half maximum (FWHM)] of the electron beam was approximately 0.5 eV which is typical of such a gun with a tungsten filament cathode. Emitted photons, corresponding to radiative decay of collisionally excited species in the target region were detected by a 0.5-meter Libert spectrometer equipped with a cooled ( $-30^{\circ}\text{C}$ ) photomultiplier detector mounted at the exit slit. The instrument was entirely automated for repetitive scans by a computer.

Two types of measurements were carried out. To obtain an emission spectrum, the electron-impact energy was fixed and the emission intensity as a function of wavelength was recorded. To obtain the onset values and initial slopes for the excitation functions, we fixed the detection wavelength and scanned the electron impact energy.

Emission spectra obtained from the  $C_{60}$  sample at 20 and 100 eV electron impact energy are shown in Fig. 1. The OH related emission features are present in both spectra while the H related emissions are absent at 20 eV (which is less than the threshold energy for these emission processes). Superficially, the emissions appear to be the same as those obtained from  $H_2O$  sample under the same experimental conditions and it would be natural to assume that background  $H_2O$  or  $H_2O$  adsorbed by (or bound to) the  $C_{60}$  sample is responsible for the observed emissions. There are several indications, however, that this was not the case. No emission was observed from the background when the crucible was heated but empty or heated at temperatures below 300°C. Heating the sample for long durations at temperatures in the 400°C to 500°C range did not eliminate these radiations. When the crucible was heated above 500°C the emission persisted until the sample in the crucible was entirely consumed or decomposed to graphite. It should be noted that in fresh samples emission appeared at temperatures between 300-400°C but as time went on the temperature had to be raised to obtain the same emission intensity. These observations were made with a variety of samples ( $C_{60}$ ,  $C_{70}$  and unseparated mixtures prepared with anhydrous toluene or benzene extractions by Materials and Electrochemical Research Corporation). No water was used in the preparation of any of these samples. It should be pointed out that we also studied toluene and benzene to investigate possible contributions of their spectra to the  $C_{60}$  spectrum. No OH type emission was found in either case, although emission from anhydrous toluene (Containing less than 0.005%  $H_2O$ ) appeared at around 280 nm. This spectral feature is, however, clearly distinguishable from the OH type emissions.

Another indication came from a closer examination of the OH type emission features as demonstrated in Fig. 2. This figure shows overplotted spectra obtained separately for  $H_2O$  and  $C_{60}$  samples under identical experimental conditions at 30 and 100 eV electron impact energies. The 1120 spectrum observed in the present study at 100 eV is

identical to that obtained by other investigators<sup>9,10</sup> as far as the relative intensity distribution of the various bands for the  $011 [A^2 \Sigma_1 (v') \rightarrow X^2 \Sigma_1 (v'')]$  transition is concerned. This intensity distribution is not significantly altered as the electron impact energy is changed. For the emission features associated with the  $C_{60}$  sample the intensity distribution differs significantly from those observed for the  $H_2O$  sample and changes significantly with impact energy.

in order to learn more about the nature of the  $C_{60}$  sample related emissions, we measured onset energy values for both the  $011$  and  $111$  type emissions. For this purpose the He ( $4^3P \rightarrow 2^3S$ ) emission feature at  $318.9\text{ nm}$  was utilized for which the onset value is  $23.71\text{ eV}$ .<sup>11</sup> Both  $C_{60}$  and He samples were introduced into the interaction region and the excitation functions at  $318.9\text{ nm}$  and at the wavelength corresponding to the desired  $C_{60}$  related feature were recorded under identical experimental conditions. The contact potential observed for the He emission was then applied to correct the observed onset energy for the  $C_{60}$  related emission. At  $315\text{ nm}$  the He emission feature overlaps the  $C_{60}$  related OH ( $1-1$ ) band with the present spectral resolution of  $5\text{ nm}$  (FWHM) and the excitation function shows two distinct steps corresponding to the two onsets. The calibration procedure was carried out also against the  $N_2 [c^3\Pi_u (v'=0) \rightarrow 13^3\Pi_g (v''=0)]$  band at  $337.1\text{ nm}$  for which the onset value of  $11.03\text{ eV}$  is known from spectroscopy of  $N_2$ .<sup>12</sup> The operation of the apparatus and the reliability of the calibration procedure were established by introducing a mixture of He and  $N_2$  into the interaction region and calibrating one against the other. In addition, the onset value was determined for  $H_2O$  sample against He and was found to be  $9.2 \pm 0.5\text{ eV}$  which is in agreement with previous measurements.<sup>9,10</sup> The conclusions drawn from these measurements can be summarized as follows:

1. The onset for the  $C_{60}$  related OH ( $0-0$ ) transition is  $11.6 \pm 0.5\text{ eV}$ .

2. The onset (within the  $\pm 0.5$  eV error limit) is the same for all  $C_{60}$  related 011 emissions.

3. The onset for the  $C_{60}$  related Balmer- $\alpha$  emission is  $20.6 \pm 1.0$  eV.

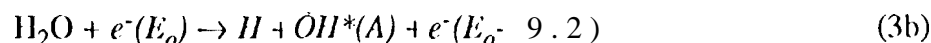
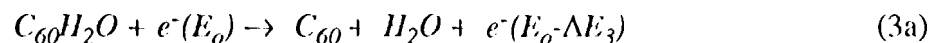
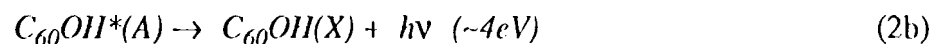
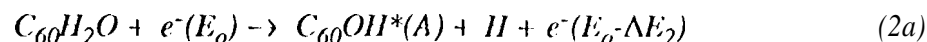
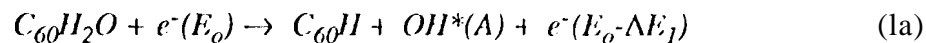
It should be pointed out that at longer wavelengths (in the visible spectral region where H I Balmer series appear), it was necessary to introduce additional apertures in the electron gun and increase the distance between the filament and the interaction region to minimize the background radiation. This resulted in decreased electron beam current and larger uncertainties (i.e.  $\pm 1.0$  eV) in the onset value measurements.

One other type of measurement was carried out to demonstrate the consistency of the onset measurements, both in their onset energy values and initial slopes of the excitation functions. The onset region of the excitation functions for (011) ((0)-0) type emission at 312.5 nm was measured for pure  $H_2O$ , for pure  $C_{60}$  sample and their mixtures under identical experimental conditions. A composite of these results is shown in Fig. 3. The excitation function for the mixture clearly shows the two distinct onsets associated with  $H_2O$  and  $C_{60}$  sample. These onsets are identical with the onsets in the pure components, both in onset value and initial shape.

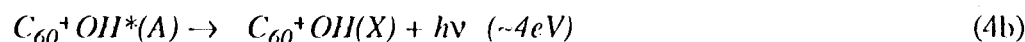
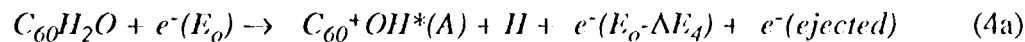
The interpretation of the present results and the assignment of the observed emissions are based on observations made in the present experiments, on mass spectroscopic studies of Wood et al.<sup>7</sup>, and on the energetics of the various processes involved (see Table 1 for pertinent energy data). It is concluded that the emissions observed from the  $C_{60}$  sample cannot be associated with 1120 and cannot be due to  $C_{60}$  molecule.

Contribution from background  $H_2O$  (water molecules adsorbed on and subsequently outgassed from various surfaces in the chamber) was not found under the

present experimental conditions. More importantly, the onset value and excitation function shape observed for the C<sub>60</sub> type OH emission are inconsistent with those of free H<sub>2</sub>O. The assumption that H<sub>2</sub>O is bound to C<sub>60</sub> can be eliminated based on energetic reasonings. The three processes to consider here, as far as the OH type emissions are concerned, are:

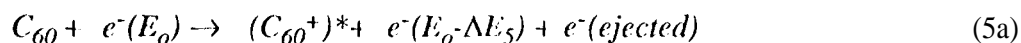


Dissociative excitation for OH(A)/H<sub>2</sub>O has a threshold of 9.2 eV. The weak van der Waals type binding between H<sub>2</sub>O and C<sub>60</sub> should not drastically change these values for the C<sub>60</sub>H<sub>2</sub>O complex. The dissociative excitation processes described by equations (1) and (2), therefore, should also have onsets near 9.2 eV and not 11.6 eV, as observed. A 2.4 eV binding energy for H<sub>2</sub>O in C<sub>60</sub> is not acceptable. The two-step process described by Eqn.(3) is very unlikely based on the two step requirement. Moreover, it is also inconsistent from the onset energy point of view. The process



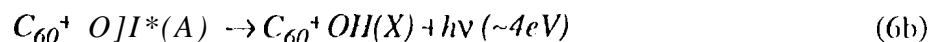
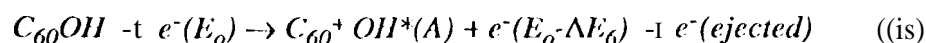
can be eliminated based on energetics.

It is apparent that the atomic type Balmer radiation cannot be due to  $C_{60}$ . The same is very much probable for the OH type radiation, based on the appearance of the emission spectrum which is clearly characteristic of the four OH bands. If one were to assume that a similar emission pattern may result  $C_{60}$  emission, one would have to consider the following process (because the ionization potential of  $C_{60}$  is  $7.54 \pm 0.04$  eV and the onset value is  $11.6 \pm 0.5$  eV):

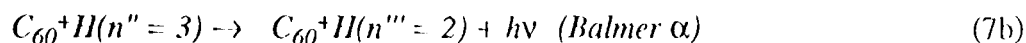
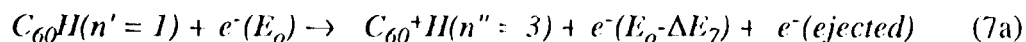


and excited atomic states which would match the OH band structure pattern. This is very unlikely.

A satisfactory and energetically consistent explanation for the observations of the OH type emission can be given by the following processes:



(The OH may or may not remain attached to  $C_{60}$ ). Similar reasonings, concerning the Balmer series emissions, lead to the only acceptable process given as



It should be noted that the mechanism described by Eqn. 7 for Balmer  $\alpha$  emission also applies to production of other members of the Balmer series ( $n'' = 4, 5, \dots$ ). A similar

mechanism (with  $n'' = 1$ ) should lead to production of the Lyman series emission in the vacuum UV region (which was not investigated in the present experiments).

These observations and interpretations reveal that the observed emissions are not associated with  $C_{60}$  but with  $C_{60}OH$  and  $C_{60}H$  adducts. These adducts are either formed during the production of buckyball samples and are not separated out by the purification process or they formed during the purification and/or subsequent sample handling processes. The existence of fullerene adducts was revealed by earlier mass spectroscopic studies. Addition of 14, 15, 16 and 17 daltons to  $C_{60}$  (and  $C_{70}$ ) was shown to be due to  $CH_2$ ,  $CH_3$ ,  $O$  and  $OH$ , respectively and positive and negative ions, associated with 0, 1 and 11 fullerene adducts, were observed in mass spectra of  $C_{60}$  ( $C_{70}$ ) samples. (For references see Wood et al.<sup>7</sup>). The mechanism to explain our observations requires simultaneous ionization of  $C_{60}$  and excitation of the weakly bound  $O$  and  $H$  species. It is fairly well established that energy deposited in condensed or dissolved  $C_{60}$  (from photon absorption or electron impact) very quickly redistributes among the internal degrees of freedom and eventually results in  $C_{60}$  in its ground and the lowest metastable states via various decay and collision processes.<sup>4</sup> The metastable species weakly radiate in the infrared (IR) spectral region.<sup>8,15</sup> The puzzling question that remains is: How does the excitation of the loosely bound  $OH$  and  $H$  occur? Further investigations involving ion/photon coincidence measurements should be carried out to answer this question and confirm the mechanism.

### Acknowledgment

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**Table 1.** Summary Of energies pertinent to the interpretation of the present observations.

Reaction	AE(eV)	Reference
$\text{H}_2\text{O} + \text{e}^- \rightarrow \text{OH}(\text{X}) + \text{H}(1\text{s})$	5.114	13
$\text{OH}(\text{A}) + \text{H}(1\text{s})$	9.2	9
$\text{OH}(\text{X}) + \text{H}(\text{n} = 3)$	17.202	13
$\text{OH}(\text{X}) \rightarrow \text{O}}](\text{A})$	4.017	13
$\text{H}(\text{n} = 3) \rightarrow \text{H}(\text{n} = 1)$	12.088	11
$\text{H}(\text{n} = 3) \rightarrow \text{H}(\text{n} = 2)$	1.889	11
$\text{C}_{60} + \text{e}^- \rightarrow \text{C}_{60}^+ + 2\text{e}^-$	7.5450.04	14
$\text{C}_{60} \text{ sample}^* + \text{e}^- \rightarrow \text{OH}(\text{A} \rightarrow \text{X}) \text{ type radiation}$	$11.6 \pm 0.5$	present result for onset
$\text{H Balmer } \alpha \text{ type radiation}$	$20.6 \pm 1.0$	present result for onset

\*The sample contains  $\text{C}_{60}\text{OH}$  and  $\text{C}_{60}\text{H}$  adducts.

### Figure Captions

**Figure 1.** Emission spectra obtained under electron impact from  $C_{60}^+OI I^*$  and  $C_{60}^+I I^*$  species at a, 20 eV and b, 100 eV impact energies.

**Figure 2.** Overplots of the  $OI \lambda$  type emission features from  $C_{60}^+OI I^*$  (.) and pure  $I I_2O$  (o) obtained at electron impact energies of a, 30 eV and b, 100 eV.

**Figure 3.** Onset energy values and initial slopes of optical excitation functions for  $O \lambda$  type emission from pure  $H_2O$  (V),  $C_{60}OH$  (V) and their mixtures (.).

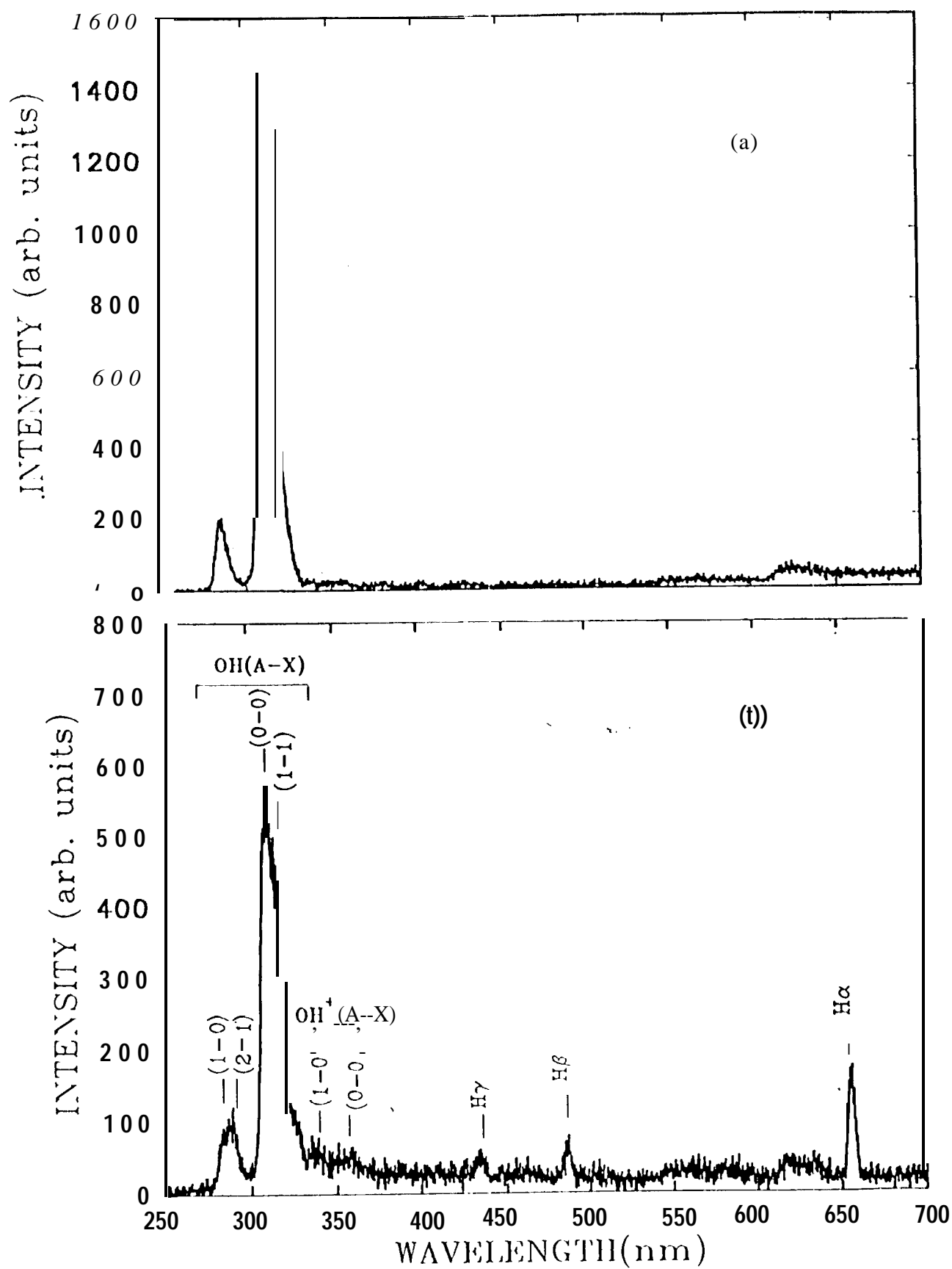


Fig. 1

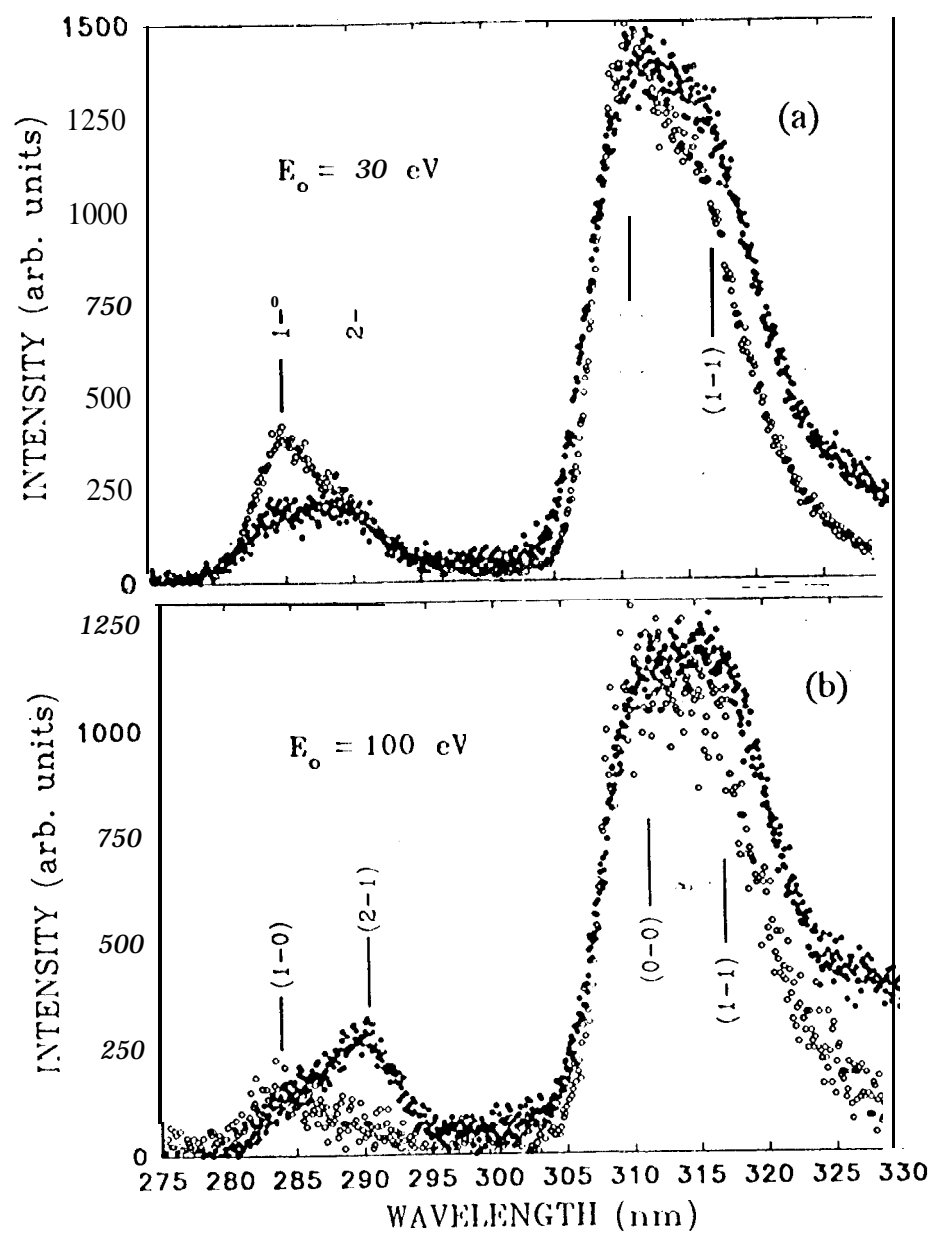


Fig. 2

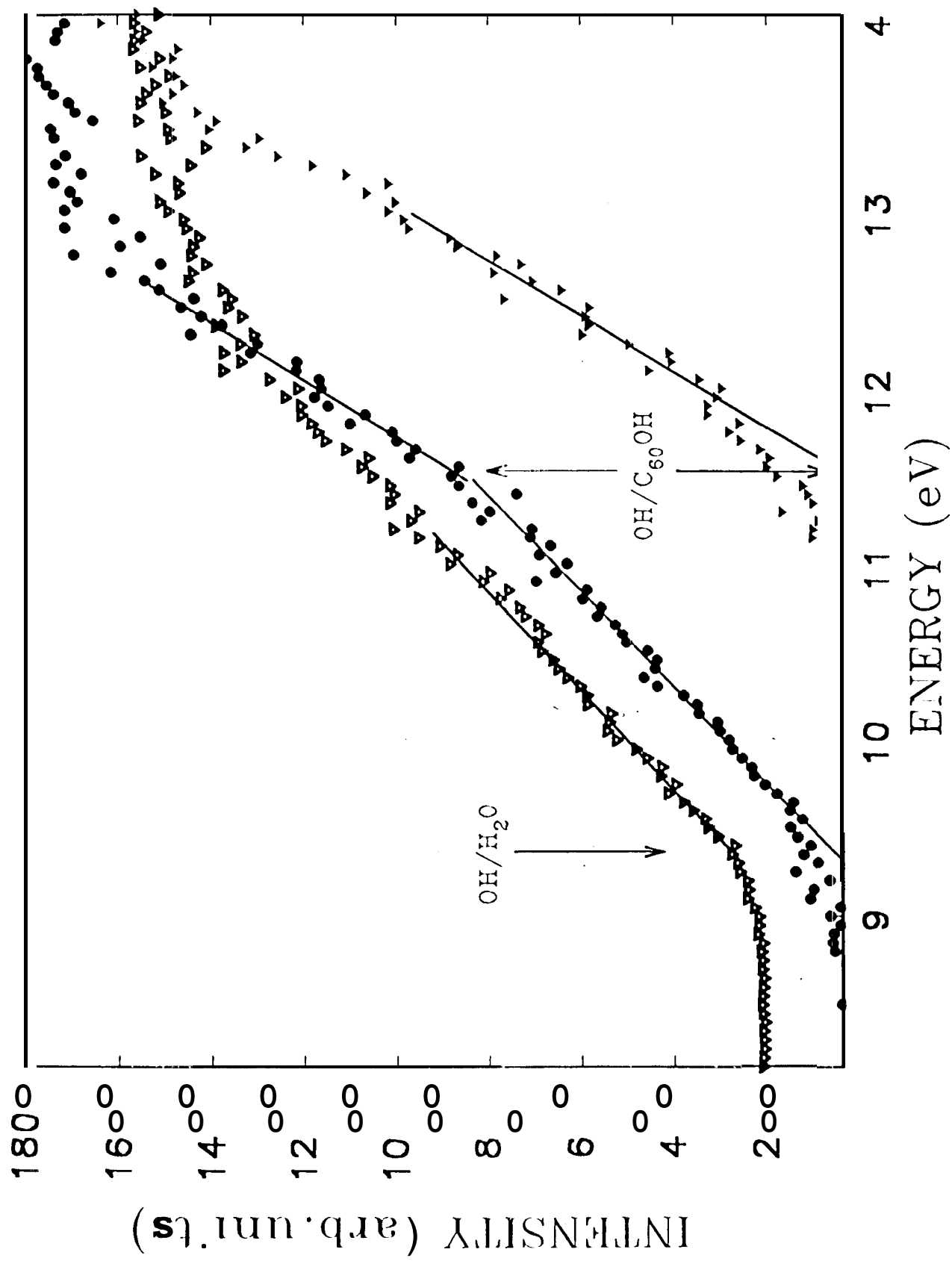


Fig. 3